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## PATENT COOPERATION TREATY

PCT

## NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Assistant Commissioner for Patents  
 United States Patent and Trademark  
 Office  
 Box PCT  
 Washington, D.C.20231  
 ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

<b>Date of mailing (day/month/year)</b> 14 June 2000 (14.06.00)	
<b>International application No.</b> PCT/DK99/00523	<b>Applicant's or agent's file reference</b> P199800998WO
<b>International filing date (day/month/year)</b> 04 October 1999 (04.10.99)	<b>Priority date (day/month/year)</b> 02 October 1998 (02.10.98)
<b>Applicant</b> GLEJBØL, Kristian et al	

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:  
 25 April 2000 (25.04.00)

☐ in a notice effecting later election filed with the International Bureau on:  
 \_\_\_\_\_

2. The election ☒ was  
☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

<b>The International Bureau of WIPO</b> 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No.: (41-22) 740.14.35	<b>Authorized officer</b> Claudio Borton Telephone No.: (41-22) 338.83.38
--	---

RECEIVED

08 NOV. 1999

Hofman-Bang & Boutard,  
Lehmann & Ree A/S

PCT

PATENT COOPERATION TREATY

SBO/PAW

From the INTERNATIONAL BUREAU

To:

HOFMAN-BANG & BOUTARD, LEHMANN &  
REE A/S  
Hans Bekkevolds Allé 7  
DK-2900 Hellerup  
DANEMARKNOTIFICATION CONCERNING  
SUBMISSION OR TRANSMITTAL  
OF PRIORITY DOCUMENT

(PCT Administrative Instructions, Section 411)

Date of mailing (day/month/year) 01 November 1999 (01.11.99)	<b>IMPORTANT NOTIFICATION</b>
Applicant's or agent's file reference P199800998WO	
International application No. PCT/DK99/00523	
International publication date (day/month/year) Not yet published	
International filing date (day/month/year) 04 October 1999 (04.10.99)	Priority date (day/month/year) 02 October 1998 (02.10.98)
Applicant N.K.T. RESEARCH CENTER A/S et al	

- The applicant is hereby notified of the date of receipt (except where the letters "NR" appear in the right-hand column) by the International Bureau of the priority document(s) relating to the earlier application(s) indicated below. Unless otherwise indicated by an asterisk appearing next to a date of receipt, or by the letters "NR", in the right-hand column, the priority document concerned was submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b).
- This updates and replaces any previously issued notification concerning submission or transmittal of priority documents.
- An asterisk(\*) appearing next to a date of receipt, in the right-hand column, denotes a priority document submitted or transmitted to the International Bureau but not in compliance with Rule 17.1(a) or (b). In such a case, the attention of the applicant is directed to Rule 17.1(c) which provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.
- The letters "NR" appearing in the right-hand column denote a priority document which was not received by the International Bureau or which the applicant did not request the receiving Office to prepare and transmit to the International Bureau, as provided by Rule 17.1(a) or (b), respectively. In such a case, the attention of the applicant is directed to Rule 17.1(c) which provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.

<u>Priority date</u>	<u>Priority application No.</u>	<u>Country or regional Office or PCT receiving Office</u>	<u>Date of receipt of priority document</u>
02 Octo 1998 (02.10.98)	PA 1998 01247	DK	29 Octo 1999 (29.10.99)

The International Bureau of WIPO  
34, chemin des Colombettes  
1211 Geneva 20, Switzerland

Facsimile No. (41-22) 740.14.35

Authorized officer

Taïeb Akreimi TA

Telephone No. (41-22) 338.83.38

AHE/cvw

PCT

From the INTERNATIONAL BUREAU

NOTICE INFORMING THE APPLICANT OF THE  
COMMUNICATION OF THE INTERNATIONAL  
APPLICATION TO THE DESIGNATED OFFICES

(PCT Rule 47.1(c), first sentence)

To:

HOFMAN-BANG & BOUTARD, LEHMANN &  
REE A/S

Hans Bekkevolds Allé 7

DK-2900 Hellerup

DANEMARK

RECEIVED

25 APR. 2000

Hofman-Bang & Boutard,  
Lehmann & Ree A/s

Date of mailing (day/month/year) 13 April 2000 (13.04.00)		
Applicant's or agent's file reference P199800998WO		IMPORTANT NOTICE
International application No. PCT/DK99/00523	International filing date (day/month/year) 04 October 1999 (04.10.99)	Priority date (day/month/year) 02 October 1998 (02.10.98)
Applicant N.K.T. RESEARCH CENTER A/S et al		

1. Notice is hereby given that the International Bureau has communicated, as provided in Article 20, the international application to the following designated Offices on the date indicated above as the date of mailing of this Notice:  
AU,CN,JP,KP,KR,US

In accordance with Rule 47.1(c), third sentence, those Offices will accept the present Notice as conclusive evidence that the communication of the international application has duly taken place on the date of mailing indicated above and no copy of the international application is required to be furnished by the applicant to the designated Office(s).

2. The following designated Offices have waived the requirement for such a communication at this time:

AE,AL,AM,AP,AT,AZ,BA,BB,BG,BR,BY,CA,CH,CU,CZ,DE,DK,DM,EA,EE,EP,ES,FI,GB,GD,GE,GH,  
GM,HR,HU,ID,IL,IN,IS,KE,KG,KZ,LC,LK,LR,LS,LT,LU,LV,MD,MG,MK,MN,MW,MX,NO,NZ,OA,PL,  
PT,RO,RU,SD,SE,SG,SI,SK,SL,TJ,TM,TR,TT,TZ,UA,UG,UZ,VN,YU,ZA,ZW

The communication will be made to those Offices only upon their request. Furthermore, those Offices do not require the applicant to furnish a copy of the international application (Rule 49.1(a-bis)).

3. Enclosed with this Notice is a copy of the international application as published by the International Bureau on  
13 April 2000 (13.04.00) under No. WO 00/20656

## REMINDER REGARDING CHAPTER II (Article 31(2)(a) and Rule 54.2)

If the applicant wishes to postpone entry into the national phase until 30 months (or later in some Offices) from the priority date, a demand for international preliminary examination must be filed with the competent International Preliminary Examining Authority before the expiration of 19 months from the priority date.

It is the applicant's sole responsibility to monitor the 19-month time limit.

Note that only an applicant who is a national or resident of a PCT Contracting State which is bound by Chapter II has the right to file a demand for international preliminary examination.

## REMINDER REGARDING ENTRY INTO THE NATIONAL PHASE (Article 22 or 39(1))

If the applicant wishes to proceed with the international application in the national phase, he must, within 20 months or 30 months, or later in some Offices, perform the acts referred to therein before each designated or elected Office.

For further important information on the time limits and acts to be performed for entering the national phase, see the Annex to Form PCT/IB/301 (Notification of Receipt of Record Copy) and Volume II of the PCT Applicant's Guide.

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer  J. Zahra
Facsimile No. (41-22) 740.14.35	Telephone No. (41-22) 338.83.38

Continuation of Form PCT/IB/308

**NOTICE INFORMING THE APPLICANT OF THE COMMUNICATION OF  
THE INTERNATIONAL APPLICATION TO THE DESIGNATED OFFICES**

<b>Date of mailing (day/month/year)</b> 13 April 2000 (13.04.00)	<b>IMPORTANT NOTICE</b>
<b>Applicant's or agent's file reference</b> P199800998WO	<b>International application No.</b> PCT/DK99/00523
<p>The applicant is hereby notified that, at the time of establishment of this Notice, the time limit under Rule 46.1 for making amendments under Article 19 has not yet expired and the International Bureau had received neither such amendments nor a declaration that the applicant does not wish to make amendments.</p>	

## PATENT COOPERATION TREATY

NRH/HK

- 3 JULI 2000

Hofman-Bang & Boutard,  
Lehmann & Ree A/S

PCT

From the INTERNATIONAL BUREAU

To:

HOFMAN-BANG A/S  
Hans Bekkevolds Allé 7  
DK-2900 Hellerup  
DANEMARKINFORMATION CONCERNING ELECTED  
OFFICES NOTIFIED OF THEIR ELECTION

(PCT Rule 61.3)

Date of mailing (day/month/year)  
14 June 2000 (14.06.00)Applicant's or agent's file reference  
P199800998WO

## IMPORTANT INFORMATION

International application No.  
PCT/DK99/00523International filing date (day/month/year)  
04 October 1999 (04.10.99)Priority date (day/month/year)  
02 October 1998 (02.10.98)

Applicant

N.K.T. RESEARCH CENTER A/S et al

1. The applicant is hereby informed that the International Bureau has, according to Article 31(7), notified each of the following Offices of its election:

AP : GH,GM,KE,LS,MW,SD,SL,SZ,TZ,UG,ZW  
 EP : AT,BE,CH,CY,DE,DK,ES,FI,FR,GB,GR,IE,IT,LU,MC,NL,PT,SE  
 National : AU,BG,BR,CA,CN,CZ,DE,IL,JP,KP,KR,MN,NO,NZ,PL,RO,RU,SE,SK,US

2. The following Offices have waived the requirement for the notification of their election; the notification will be sent to them by the International Bureau only upon their request:

EA : AM,AZ,BY,KG,KZ,MD,RU,TJ,TM  
 OA : BF,BJ,CF,CG,CI,CM,GA,GN,GW,ML,MR,NE,SN,TD,TG  
 National : AE,AL,AM,AT,AZ,BA,BB,BY,CH,CU,DK,DM,EE,ES,FI,GB,GD,GE,GH,GM,HR,  
 HU,ID,IN,IS,KE,KG,KZ,LC,LK,LR,LS,LT,LU,LV,MD,MG,MK,MW,MX,PT,SD,SG,SI,SL,  
 TJ,TM,TR,TT,TZ,UA,UG,UZ,VN,YU,ZA,ZW

3. The applicant is reminded that he must enter the "national phase" before the expiration of 30 months from the priority date before each of the Offices listed above. This must be done by paying the national fee(s) and furnishing, if prescribed, a translation of the international application (Article 39(1)(a)), as well as, where applicable, by furnishing a translation of any annexes of the international preliminary examination report (Article 36(3)(b) and Rule 74.1).

Some offices have fixed time limits expiring later than the above-mentioned time limit. For detailed information about the applicable time limits and the acts to be performed upon entry into the national phase before a particular Office, see Volume II of the PCT Applicant's Guide.

The entry into the European regional phase is postponed until 31 months from the priority date for all States designated for the purposes of obtaining a European patent.

The International Bureau of WIPO  
 34, chemin des Colombettes  
 1211 Geneva 20, Switzerland

Facsimile No. (41-22) 740.14.35

Authorized officer:

Claudio Borton

Telephone No. (41-22) 338.83.38

PCT

REQUEST

**CONFIRMATION COPY**

The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty.

For receiving Office use only

International Application No.

International Filing Date

Name of receiving Office and "PCT International Application"

Applicant's or agent's file reference  
(if desired) (12 characters maximum) P199800998 WO**Box No. I TITLE OF INVENTION**

A method of metallizing the surface of a solid polymer substrate and the product obtained

**Box No. II APPLICANT**

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

N.K.T. Research Center A/S  
Priorparken 878  
DK-2605 Brøndby  
Denmark

☐ This person is also inventor.

Telephone No.  
(45) 43 48 35 00

Facsimile No.  
(45) 43 63 00 99

Teleprinter No.

State (that is, country) of nationality:

DK Denmark

State (that is, country) of residence:

DK Denmark

This person is applicant  
for the purposes of:
☐ all designated  
States

☒ all designated States except  
the United States of America

☐ the United States  
of America only

☐ the States indicated in  
the Supplemental Box
**Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)**

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

GLEJBØL, Kristian  
Fiskerhusene 8  
DK-2620 Albertslund  
Denmark

This person is:

☐ applicant only

☒ applicant and inventor

☐ inventor only (If this check-box  
is marked, do not fill in below.)

State (that is, country) of nationality:

DK Denmark

State (that is, country) of residence:

DK Denmark

This person is applicant  
for the purposes of:
☐ all designated  
States

☐ all designated States except  
the United States of America

☒ the United States  
of America only

☐ the States indicated in  
the Supplemental Box

☒ Further applicants and/or (further) inventors are indicated on a continuation sheet.
**Box No. IV AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE**

The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent International Authorities as:

☒ agent

☐ common representative

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)

Hofman-Bang & Boutard, Lehmann & Ree A/S  
Hans Bekkevolds Allé 7  
DK-2900 Hellerup  
Denmark

Telephone No.

(45) 39 48 80 00

Facsimile No.

(45) 39 48 80 80

Teleprinter No.

☐ Address for correspondence: Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent.

## Continuation of Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)

*If none of the following sub-boxes is used, this sheet should not be included in the request.*

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

WINTHER-JENSEN, Bjørn  
Hornemannsgade 17  
DK-2100 Copenhagen Ø  
Denmark

This person is:

- ☐ applicant only  
☒ applicant and inventor  
☐ inventor only (If this check-box is marked, do not fill in below.)

State (that is, country) of nationality:  
DK Denmark

State (that is, country) of residence:  
DK Denmark

This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

This person is:

- ☐ applicant only  
☐ applicant and inventor  
☐ inventor only (If this check-box is marked, do not fill in below.)

State (that is, country) of nationality:

State (that is, country) of residence:

This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

This person is:

- ☐ applicant only  
☐ applicant and inventor  
☐ inventor only (If this check-box is marked, do not fill in below.)

State (that is, country) of nationality:

State (that is, country) of residence:

This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

This person is:

- ☐ applicant only  
☐ applicant and inventor  
☐ inventor only (If this check-box is marked, do not fill in below.)

State (that is, country) of nationality:

State (that is, country) of residence:

This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

☐ Further applicants and/or (further) inventors are indicated on another continuation sheet.



**Box No.V DESIGNATION OF STATES**

The following designations are hereby made under Rule 4.9(a) (mark the applicable check-boxes; at least one must be marked):

**Regional Patent**

- ☒ **AP** ARIPO Patent: GH Ghana, GM Gambia, KE Kenya, LS Lesotho, MW Malawi, SD Sudan, SZ Swaziland, UG Uganda, ZW Zimbabwe, and any other State which is a Contracting State of the Harare Protocol and of the PCT
- ☒ **EA** Eurasian Patent: AM Armenia, AZ Azerbaijan, BY Belarus, KG Kyrgyzstan, KZ Kazakhstan, MD Republic of Moldova, RU Russian Federation, TJ Tajikistan, TM Turkmenistan, and any other State which is a Contracting State of the Eurasian Patent Convention and of the PCT
- ☒ **EP** European Patent: AT Austria, BE Belgium, CH and LI Switzerland and Liechtenstein, CY Cyprus, DE Germany, DK Denmark, ES Spain, FI Finland, FR France, GB United Kingdom, GR Greece, IE Ireland, IT Italy, LU Luxembourg, MC Monaco, NL Netherlands, PT Portugal, SE Sweden, and any other State which is a Contracting State of the European Patent Convention and of the PCT
- ☒ **OA** OAPI Patent: BF Burkina Faso, BJ Benin, CF Central African Republic, CG Congo, CI Côte d'Ivoire, CM Cameroon, GA Gabon, GN Guinea, GW Guinea-Bissau, ML Mali, MR Mauritania, NE Niger, SN Senegal, TD Chad, TG Togo, and any other State which is a member State of OAPI and a Contracting State of the PCT (if other kind of protection or treatment desired, specify on dotted line) .....

**National Patent (if other kind of protection or treatment desired, specify on dotted line):**

- |   |   |
|---|---|
| <input checked="" type="checkbox"/> <b>AL</b> Albania .....                                     | <input checked="" type="checkbox"/> <b>LS</b> Lesotho .....                                   |
| <input checked="" type="checkbox"/> <b>AM</b> Armenia .....                                     | <input checked="" type="checkbox"/> <b>LT</b> Lithuania .....                                 |
| <input checked="" type="checkbox"/> <b>AT</b> Austria .....                                     | <input checked="" type="checkbox"/> <b>LU</b> Luxembourg .....                                |
| <input checked="" type="checkbox"/> <b>AU</b> Australia .....                                   | <input checked="" type="checkbox"/> <b>LV</b> Latvia .....                                    |
| <input checked="" type="checkbox"/> <b>AZ</b> Azerbaijan .....                                  | <input checked="" type="checkbox"/> <b>MD</b> Republic of Moldova .....                       |
| <input checked="" type="checkbox"/> <b>BA</b> Bosnia and Herzegovina .....                      | <input checked="" type="checkbox"/> <b>MG</b> Madagascar .....                                |
| <input checked="" type="checkbox"/> <b>BB</b> Barbados .....                                    | <input checked="" type="checkbox"/> <b>MK</b> The former Yugoslav Republic of Macedonia ..... |
| <input checked="" type="checkbox"/> <b>BG</b> Bulgaria .....                                    | <input checked="" type="checkbox"/> <b>MN</b> Mongolia .....                                  |
| <input checked="" type="checkbox"/> <b>BR</b> Brazil .....                                      | <input checked="" type="checkbox"/> <b>MW</b> Malawi .....                                    |
| <input checked="" type="checkbox"/> <b>BY</b> Belarus .....                                     | <input checked="" type="checkbox"/> <b>MX</b> Mexico .....                                    |
| <input checked="" type="checkbox"/> <b>CA</b> Canada .....                                      | <input checked="" type="checkbox"/> <b>NO</b> Norway .....                                    |
| <input checked="" type="checkbox"/> <b>CH</b> and <b>LI</b> Switzerland and Liechtenstein ..... | <input checked="" type="checkbox"/> <b>NZ</b> New Zealand .....                               |
| <input checked="" type="checkbox"/> <b>CN</b> China .....                                       | <input checked="" type="checkbox"/> <b>PL</b> Poland .....                                    |
| <input checked="" type="checkbox"/> <b>CU</b> Cuba .....  | <input checked="" type="checkbox"/> <b>PT</b> Portugal .....                                  |
| <input checked="" type="checkbox"/> <b>CZ</b> Czech Republic .....                              | <input checked="" type="checkbox"/> <b>RO</b> Romania .....                                   |
| <input checked="" type="checkbox"/> <b>DE</b> Germany .....                                     | <input checked="" type="checkbox"/> <b>RU</b> Russian Federation .....                        |
| <input checked="" type="checkbox"/> <b>DK</b> Denmark .....                                     | <input checked="" type="checkbox"/> <b>SD</b> Sudan .....                                     |
| <input checked="" type="checkbox"/> <b>EE</b> Estonia .....                                     | <input checked="" type="checkbox"/> <b>SE</b> Sweden .....                                    |
| <input checked="" type="checkbox"/> <b>ES</b> Spain .....                                       | <input checked="" type="checkbox"/> <b>SG</b> Singapore .....                                 |
| <input checked="" type="checkbox"/> <b>FI</b> Finland .....                                     | <input checked="" type="checkbox"/> <b>SI</b> Slovenia .....                                  |
| <input checked="" type="checkbox"/> <b>GB</b> United Kingdom .....                              | <input checked="" type="checkbox"/> <b>SK</b> Slovakia .....                                  |
| <input checked="" type="checkbox"/> <b>GD</b> Grenada .....                                     | <input checked="" type="checkbox"/> <b>SL</b> Sierra Leone .....                              |
| <input checked="" type="checkbox"/> <b>GE</b> Georgia .....                                     | <input checked="" type="checkbox"/> <b>TJ</b> Tajikistan .....                                |
| <input checked="" type="checkbox"/> <b>GH</b> Ghana .....                                       | <input checked="" type="checkbox"/> <b>TM</b> Turkmenistan .....                              |
| <input checked="" type="checkbox"/> <b>GM</b> Gambia .....                                      | <input checked="" type="checkbox"/> <b>TR</b> Turkey .....                                    |
| <input checked="" type="checkbox"/> <b>HR</b> Croatia .....                                     | <input checked="" type="checkbox"/> <b>TT</b> Trinidad and Tobago .....                       |
| <input checked="" type="checkbox"/> <b>HU</b> Hungary .....                                     | <input checked="" type="checkbox"/> <b>UA</b> Ukraine .....                                   |
| <input checked="" type="checkbox"/> <b>ID</b> Indonesia .....                                   | <input checked="" type="checkbox"/> <b>UG</b> Uganda .....                                    |
| <input checked="" type="checkbox"/> <b>IL</b> Israel .....                                      | <input checked="" type="checkbox"/> <b>US</b> United States of America .....                  |
| <input checked="" type="checkbox"/> <b>IN</b> India .....                                       | <input checked="" type="checkbox"/> <b>UZ</b> Uzbekistan .....                                |
| <input checked="" type="checkbox"/> <b>IS</b> Iceland .....                                     | <input checked="" type="checkbox"/> <b>VN</b> Viet Nam .....                                  |
| <input checked="" type="checkbox"/> <b>JP</b> Japan .....                                       | <input checked="" type="checkbox"/> <b>YU</b> Yugoslavia .....                                |
| <input checked="" type="checkbox"/> <b>KE</b> Kenya .....                                       | <input checked="" type="checkbox"/> <b>ZW</b> Zimbabwe .....                                  |
| <input checked="" type="checkbox"/> <b>KG</b> Kyrgyzstan .....                                  |   |
| <input checked="" type="checkbox"/> <b>KP</b> Democratic People's Republic of Korea .....       |   |

Check-boxes reserved for designating States (for the purposes of a national patent) which have become party to the PCT after issuance of this sheet:

- |   |  |
|---|--|
| <input checked="" type="checkbox"/> <b>KR</b> Republic of Korea ..... | <input checked="" type="checkbox"/> <b>AE</b> United Arab Emirates .....                         |
| <input checked="" type="checkbox"/> <b>KZ</b> Kazakhstan .....        | <input checked="" type="checkbox"/> <b>ZA</b> South Africa .....                                 |
| <input checked="" type="checkbox"/> <b>LC</b> Saint Lucia .....       | <input checked="" type="checkbox"/> <b>TZ</b> United Rep. of Tanzania + <b>DM</b> Dominica ..... |
| <input checked="" type="checkbox"/> <b>LK</b> Sri Lanka .....         |  |
| <input checked="" type="checkbox"/> <b>LR</b> Liberia .....           |  |

**Precautionary Designation Statement:** In addition to the designations made above, the applicant also makes under Rule 4.9(b) all other designations which would be permitted under the PCT except any designation(s) indicated in the Supplemental Box as being excluded from the scope of this statement. The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit. (Confirmation of a designation consists of the filing of a notice specifying that designation and the payment of the designation and confirmation fees. Confirmation must reach the receiving Office within the 15-month time limit.)

<b>Box No. VI PRIORITY CLAIM</b>		<input type="checkbox"/> Further priority claims are indicated in the Supplemental Box.		
Filing date of earlier application (day/month/year)	Number of earlier application	Where earlier application is:		
		national application: country	regional application: regional Office	international application: receiving Office
item (1) 02.10.98 2 October 1998	PA 1998 01247	DK Denmark		
item (2)				
item (3)				

☐ The receiving Office is requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) (only if the earlier application was filed with the Office which for the purposes of the present international application is the receiving Office) identified above as item(s):

\* Where the earlier application is an ARIPO application, it is mandatory to indicate in the Supplemental Box at least one country party to the Paris Convention for the Protection of Industrial Property for which that earlier application was filed (Rule 4.10(b)(ii)). See Supplemental Box.

**Box No. VII INTERNATIONAL SEARCHING AUTHORITY**

Choice of International Searching Authority (ISA) (if two or more International Searching Authorities are competent to carry out the international search, indicate the Authority chosen; the two-letter code may be used):

ISA / SE

Request to use results of earlier search; reference to that search (if an earlier search has been carried out by or requested from the International Searching Authority):

Date (day/month/year)	Number	Country (or regional Office)
19 October 1998	DK 98/01247 (9800162)	DK Denmark

**Box No. VIII CHECK LIST; LANGUAGE OF FILING**

This international application contains the following number of sheets:

request	:	4
description (excluding sequence listing part)	:	13
claims	:	4
abstract	:	1
drawings	:	
sequence listing part of description	:	
<b>Total number of sheets</b>	:	<b>22</b>

This international application is accompanied by the item(s) marked below:

1. ☒ fee calculation sheet
2. ☐ separate signed power of attorney
3. ☐ copy of general power of attorney; reference number, if any:
4. ☐ statement explaining lack of signature
5. ☐ priority document(s) identified in Box No. VI as item(s):
6. ☐ translation of international application into (language):
7. ☐ separate indications concerning deposited microorganism or other biological material
8. ☐ nucleotide and/or amino acid sequence listing in computer readable form
9. ☒ other (specify): Copy of ITS DK 98/01247 (9800162)

Figure of the drawings which should accompany the abstract:

Language of filing of the international application: English

**Box No. IX SIGNATURE OF APPLICANT OR AGENT**

Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the request).

N.K.T. Research Center A/S

Kristian Glejbøl

Bjørn Winther-Jensen

For receiving Office use only	
1. Date of actual receipt of the purported international application:	2. Drawings:  <input type="checkbox"/> received:  <input type="checkbox"/> not received:
3. Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application:	
4. Date of timely receipt of the required corrections under PCT Article 11(2):	
5. International Searching Authority (if two or more are competent): ISA /	6. <input type="checkbox"/> Transmittal of search copy delayed until search fee is paid.

For International Bureau use only
Date of receipt of the record copy by the International Bureau:

**Box No. VI PRIORITY CLAIM**☐ Further priority claims are indicated in the Supplemental Box.

Filing date of earlier application (day/month/year)	Number of earlier application	Where earlier application is:		
		national application: country	regional application:* regional Office	international application: receiving Office
item (1) 02.10.98 2 October 1998	PA 1998 01247	DK Denmark		
item (2)				
item (3)				

☐ The receiving Office is requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) (only if the earlier application was filed with the Office which for the purposes of the present international application is the receiving Office) identified above as item(s):

\* Where the earlier application is an ARIPO application, it is mandatory to indicate in the Supplemental Box at least one country party to the Paris Convention for the Protection of Industrial Property for which that earlier application was filed (Rule 4.10(b)(ii)). See Supplemental Box.

**Box No. VII INTERNATIONAL SEARCHING AUTHORITY**

**Choice of International Searching Authority (ISA)**  
(if two or more International Searching Authorities are competent to carry out the international search, indicate the Authority chosen; the two-letter code may be used):

ISA / SE

**Request to use results of earlier search; reference to that search (if an earlier search has been carried out by or requested from the International Searching Authority):**

Date (day/month/year)

Number

Country (or regional Office)

19 October 1998

DK 98/01247

DK Denmark

- (9800162)

**Box No. VIII CHECK LIST; LANGUAGE OF FILING**

This international application contains the following number of sheets:

request : 4  
description (excluding  
sequence listing part) : 13  
claims : 4  
abstract : 1  
drawings :  
sequence listing part  
of description :  
Total number of sheets : 22

This international application is accompanied by the item(s) marked below:

1. ☒ fee calculation sheet
2. ☐ separate signed power of attorney
3. ☐ copy of general power of attorney; reference number, if any
4. ☐ statement explaining lack of signature
5. ☐ priority document(s) identified in Box No. VI as item(s):
6. ☐ translation of international application into (language):
7. ☐ separate indications concerning deposited microorganism or other biological material
8. ☐ nucleotide and/or amino acid sequence listing in computer readable form
9. ☒ other (specify): Copy of ITS DK 98/01247 (9800162)


Figure of the drawings which should accompany the abstract:


Language of filing of the


international application: English

**Box No. IX SIGNATURE OF APPLICANT OR AGENT**

Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the request).

  
N.K.T. Research Center A/S  
(Søren Isaksen, Managing  
Director)

  
Kristian Glejbøl

  
Bjørn Winther-Jensen

For receiving Office use only

1. Date of actual receipt of the purported international application:	2. Drawings:  <input type="checkbox"/> received:  <input type="checkbox"/> not received:
3. Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application:	
4. Date of timely receipt of the required corrections under PCT Article 11(2):	
5. International Searching Authority (if two or more are competent): ISA /	6. <input type="checkbox"/> Transmittal of search copy delayed until search fee is paid.

For International Bureau use only

Date of receipt of the record copy  
by the International Bureau:

From the  
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

HOFMAN-BANG & BOUTARD,  
LEHMANN & REE A/S  
Hans Bekkevolds Allé 7  
2900 Hellerup  
DANEMARK

RECEIVED

15 JAN. 2001

Hofman-Bang & Boutard,  
Lehmann & Ree A/s

PCT

NOTIFICATION OF TRANSMITTAL OF  
THE INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT

(PCT Rule 71.1)

Date of mailing  
(day/month/year) 12.01.2001

Applicant's or agent's file reference  
P199800998 WO

IMPORTANT NOTIFICATION

International application No.  
PCT/DK99/00523

International filing date (day/month/year)  
04/10/1999

Priority date (day/month/year)  
02/10/1998

Applicant  
NKT RESEARCH CENTER A/S

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

Name and mailing address of the IPEA/

 European Patent Office  
D-80298 Munich  
Tel. +49 89 2399 - 0 Tx: 523656 epmu d  
Fax: +49 89 2399 - 4465

Authorized officer

Krage, D

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## INTERNATIONAL SEARCH REPORT

International Application No.

PCT/DK 99/00523

## A. CLASSIFICATION OF SUBJECT MATTER

C23C18/20, C23C14/20, C23C18/54, C25D5/56

According to International Patent Classification (IPC) or to both national classification and IPC 7

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C23C, C25D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 97/37844 A (SIGMA LABORATORIES OF ARIZONA, INC.) 16 October 1997, the whole document.	1-17
A	EP 0640474 A (FRAUNHOFER-GESELLSCHAFT ZUR FÖRDERUNG DER ANGEWANDTEN FORSCHUNG E.V.) 01 March 1995, the whole document.	1-17
A	US 5288541 A (BLACKWELL ET AL.) 22 February 1994, the whole document.	1-17
A	DATABASE WPI, week 198935,	1

☒ Further documents are listed in the continuation of box C.☐ Patent family members are listed in annex.

## \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- \*Z\* document member of the same patent family

Date of the actual completion of the international search

25 January 2000

Date of mailing of the international search report

14.03.00

Name and mailing address of the ISA

European Patent Office, P.O. 5818 Patentaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-7040, Tx. 31 651 epo nl,  
FAX (+31-70) 340-3016

Authorized officer

BECK e.h.

EL72821183405

# INTERNATIONAL SEARCH REPORT

Intern. Application No.

PCT/DK 99/00523

- 2 -

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	<p>Derwent Publications Ltd.,  London, GB, Class G11B,  AN 1989-252964;  &amp; JP 01 184741 A (FUJITSU  LTD) 27 July 1989,  abstract.</p> <p>-----</p>	

**ANHANG**

Zum internationalen Recherchenbericht über die internationale Patentanmeldung Nr.

In diesem Anhang sind die Mitglieder der Patentfamilien der im obengenannten internationalen Recherchenbericht angeführten Patentdokumente angegeben. Diese Angaben dienen nur zur Unterrichtung und erfolgen ohne Gewähr.

**ANNEX**

To the International Search Report to the international Patent Application No.

PCT/DK 99/00523 SAE 250331

This annex lists the patent family members relating to the patent documents cited in the above-mentioned search report. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

**ANNEXE**

Au rapport de recherche international relatif à la demande de brevet international n°

La présente annexe indique les membres de la famille de brevets relatifs aux documents de brevets cités dans le rapport de recherche international visée ci-dessus. Les renseignements fournis sont donnés à titre indicatif et n'engagent pas la responsabilité de l'Office.

Im Recherchenbericht angeführte Patentdokumente Patent document cited in search report Document de brevet cité dans le rapport de recherche			Datum der Veröffentlichung Publication date Date de publication		Mitglied(er) der Patentfamilie Patent family member(s) Membre(s) de la famille de brevets		Datum der Veröffentlichung Publication date Date de publication	
WO	A1	9737844	16-10-1997		EP	A1	842046	20-05-1998
					JP	T2	10507705	28-07-1998
EP	A1	640474	01-03-1995		DE	A1	4328767	02-03-1995
					DE	C2	4328767	31-08-1995
					JP	A2	7195649	01-08-1995
					US	A	5895723	20-04-1999
US	A	5288541	22-02-1994		US	A	5525369	11-06-1996
JP	A2	1184741	24-07-1989				none	

## PATENT COOPERATION TREATY

## PCT

## INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)


Applicant's or agent's file reference <b>P199800998 WO</b>		<b>FOR FURTHER ACTION</b> See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. <b>PCT/DK99/00523</b>	International filing date (day/month/year) <b>04/10/1999</b>	Priority date (day/month/year) <b>02/10/1998</b>	
International Patent Classification (IPC) or national classification and IPC <b>C23C18/20</b>			
Applicant <b>NKT RESEARCH CENTER A/S</b>			

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 4 sheets, including this cover sheet.
  - ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 6 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☐ Certain observations on the international application

Date of submission of the demand  <b>25/04/2000</b>	Date of completion of this report  <b>12.01.2001</b>
Name and mailing address of the international preliminary examining authority:   <b>European Patent Office</b> <b>D-80298 Munich</b> <b>Tel. +49 89 2399 - 0 Tx: 523656 epmu d</b> <b>Fax: +49 89 2399 - 4465</b>	Authorized officer  <b>Brisson, O</b>  Telephone No. <b>+49 89 2399 8449</b>





# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/DK99/00523

## I. Basis of the report

1. This report has been drawn on the basis of *(substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments (Rules 70.16 and 70.17).):*

### Description, pages:

1,3,4,6-13	as originally filed			
2	as received on	21/09/2000	with letter of	21/09/2000
5	as received on	07/12/2000	with letter of	07/12/2000

### Claims, No.:

1-16	as received on	07/12/2000	with letter of	07/12/2000
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2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☒ the claims, Nos.: 17
- ☐ the drawings, sheets:

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. PCT/DK99/00523

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

*(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)*

6. Additional observations, if necessary:

**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

1. Statement

Novelty (N)	Yes:	Claims	1-16
	No:	Claims	
Inventive step (IS)	Yes:	Claims	1-16
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-16
	No:	Claims	

2. Citations and explanations  
**see separate sheet**

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

---

International application No. PCT/DK99/00523

**Re Item V**

**Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

1. Reference is made to the following document:

D1: WO 97 37844 A (SIGMA LABORATORIES OF ARIZONA, INC.) 16 October 1997,

2. Document D1, which is considered to represent the most relevant state of the art, discloses (cf. page 4, line 23 to page 5, line 4 and fig.1) a process which differs from the subject-matter of present claim 1 in that this process is specifically adapted for metallizing polymer films. Therefore, the subject-matter of claim 1 is considered as novel over D1.

3. Such metallized films according to D1 are produced in a continuous process. On the contrary, metallized injection moulded polymer components of the present application are produced one by one as discrete items. As the manufacturing methods and the products obtained are different, it does not seem to be obvious to replace a polymer film with an injection moulded polymer component in the method described in D1. Therefore, the features of the process claim 1 and the product claim 16 are considered to involve an inventive step in the sens of Article 33(3) PCT.

21-09-2000

DK 009900523

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sists of a number of small sparks created between the substrate surface and a counter electrode (a silent discharge). Most often this treatment is carried out in ambient atmosphere, and results in erosion of the surface as well as in a generation of free radicals due the energy density of the discharges and the reactivity of the atmosphere. One of the problems regarding this method is, that it is not suited for treatment prior to metallizing strongly curved surfaces or surfaces with many cavities. Other problems relate to the limited control over the resulting chemical composition of the surface.

Often a simple corona treatment is not sufficient and more specialised methods has to be employed to ensure a sufficient adhesion.

One possible method is described in WO 97/37844, where a method to obtain a coupling layer between the surface to be plated and the plated metal-film is described. According to WO 97/37844, the coupling layer is formed by vacuum deposition of a monomer on the surface, which is subsequently polymerised by an irradiation process. To ensure a good coupling between the surface and the coupling layer, and between the coupling layer and the plated metal film, plasma-treatment can be used. This process is especially suited for treatment of polymer films of infinite lengths, as the different processes (plasma-treatment, deposition of coupling layer and polymerisation of coupling layer) are carried out at different, separate, stations.

The nature of this process makes it furthermore not suitable for treatment of fluorine containing polymers like poly-tetra-fluoro-ethylene (PTFE).

35

fluoro

*9 of an injection moulded polymer component*

These objects are achieved by a method of metallizing a surface of a solid polymer substrate<sup>9</sup> comprising the steps of

5 a) generating radicals on the substrate surface by subjecting it to a gas plasma,

b) forming a layer on the surface using a plasma enhanced polymerisation process employing one or more monomers  
10 comprising monomers selected among cyano acrylate, mono- and diacrylates, such as acrylic acid, triethylen glycol diacrylat, glycidyl acrylat, isocyanates, such as 1,4-diisocyanobutane, toluenediisocyanate, epoxy compounds, such as glycidyl methacrylate, preferably 2,3-epoxypropyl  
15 methacrylat, allylic and vinylic compounds, such as vinyl acetic acid, vinyl norbonene, vinyl pyrrolidone, vinyl trimethoxysilane, vinyl trimethylsilane allylene, allyl alcohol, allyloxymethylsilane, allylphenol, allylurea 1-allyltheourea(thiosine-amine), vinyl-amine, vinyl-alcohol  
20 or allyl-amine.

c) providing a short surface deposition using a PVD or CVD process to deposit metal atoms, such as copper, tin, silver palladium, platinum, or gold

25

d) optionally providing a metallization of the surface by using a conventional electroless bath, or

avoiding electroless metallization by using direct electrolytic metallization, when the metal layer formed in c) has a thickness allowing electrolytic metallization.  
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Step b) may start before step a) provided that step b) does not terminate until step a) is started, simultaneously with step a), under step a), or follow immediately after step a). Step c) may start before step b), simulta-  
35

9 of an injection moulded polymer component

CLAIMS.

1. A method of metallizing a solid polymer substrate comprising the steps of

- a) generating radicals on the substrate surface by subjecting it to a gas plasma,
- b) forming a layer on the surface using a plasma enhanced polymerisation process employing one or more monomers comprising monomers selected among cyano acrylate, mono- and diacrylates, such as acrylic acid, triethyleneglycol diacrylate, glycidyl acrylate, isocyanates, ~~such as~~ 1,4-diisocyanobutane, toluenediisocyanate, epoxy compounds, such as glycidyl methacrylate, preferably 2,3-epoxypropyl methacrylate, allylic and vinylic compounds, ~~such as~~ vinyl acetic acid, vinyl norbornene, vinyl pyrrolidone, vinyl trimethoxysilane, vinyl trimethylsilane allylene, allyl alcohol, allyloxymethylsilane, allylphenol, allylurea, 1-allyltheourea (thiosineamine),
- c) providing a short surface deposition using a PVD or CVD process to deposit metal atoms, such as copper, tin, silver palladium, platinum, or gold, and
- d) optionally providing a metallization of the surface by using a conventional electroless bath, or avoiding electroless metallization by using direct electrolytic metallization, when the metal layer formed in c) has a thickness allowing electrolytic metallization.

2. A method according to claim 1, wherein the (catalytic metal) comprises Pt, Ag, Pd, Cu and Au.

2 x 1 → preferably selected from the group consisting of  
(-) metal layer

3. A method according to claim 1, wherein the monomer or monomer mixture comprises one or more of cyanoacrylate and glycidyl metacrylate, preferably 2,3-epoxypropyl methacrylate.

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4. A method according to each of the preceding claims 1, 2 or 3, wherein step b) comprises treatment of the surface with a monomer vapour comprising 0.5 to 90 mole-%, preferably between 10 and 60 mole % of 2-ethyl cyano acrylate vapour.

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5. A method according to claim 4, wherein the monomer prior to the vaporisation consists essentially of 2-ethyl cyano acrylate, an acid having a partial vapour pressure in the plasma which is lower than the partial vapour pressure of 2-ethyl cyano-acrylate, and up to 40 weight-% of another filler, preferably an acid having a partial vapour pressure in the plasma which is lower than half the partial vapour pressure of 2-ethyl cyano-acrylate, most preferably the acid is a polyphosphoric acid and is present prior to the vaporisation in a concentration up to 10 weight-%.

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6. A method according to each of the preceding claims, wherein the polymer substrate is a polyolefine type, such as PE, PP, or an aryl type, such as styrene, a diene type, such as polybutadiene, polyisoprene, a silicone type, such as silicone rubber, a fluorine type, such as polytetrafluorethylene or its copolymers.

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30

7. A method according to each of the preceding claims 1-5, wherein the polymer substrate is a PTFE (and) PP. (-) or

~~8. A method according to each of the preceding claims,~~  
75 wherein the polymer-substrate is an injection moulded > "

~~polymer component, a polymer fibre, a polymer thread or a polymer filler.~~ 7 ad

- 8 9. A method according to each of the preceding claims,  
5 wherein step a) comprises the generation of radicals by use of a gas plasma generated by excitation of the gas in a direct current (DC), low frequency (LF), audio frequency (AF), radio frequency (RF) or microwave generated electric field.
- 10 9 10. A method according to each of the preceding claims,  
wherein the monomer pressure in step b) is between 0.1 and 100000 Pa, preferably between 10 and 1000 Pa.
- 10 11 11. A method according to each of the preceding claims,  
15 wherein the generation step a) is carried out for a period of between 0.01 and 1000 seconds, and the treatment step b) is carried out for a period of between 0.1 and 1000 seconds.
- 20 11 12. A method according to claim N, wherein step a) is carried out for more than 30 seconds, and step b) is started 10 to 30 seconds after step a).
- 25 12 13. A method according claim N, wherein the generation step a) is carried out for a period of between 10 and 60 seconds, and the treatment step b) is carried out for a period of between 10 and 200 seconds.
- 30 13 14. A method according to each of the preceding claims, wherein the temperature is the same under both step a) and step b), and preferably the temperature under both step a) and step b) is between 250 and 450 K, most preferably between 280 and 330 K.



14 15. A method according to each of the preceding claims,  
wherein the total pressure under step a) is equal to the  
total pressure under step b), the total pressure is pref-  
erably between 0.2 and 100000 Pa, more preferably between  
s 0.2 and 10000 Pa, and most preferably between 10 and 1000  
Pa.

15 16. A method according to claim 1, where step b) starts  
before step a) provided that step b) does not terminate  
10 until step a) is started, simultaneously with step a),  
under step a), or follows immediately after step a),  
where step c) starts before step b), simultaneously with  
step b), follows immediately after step b) or within 6  
months after step b), preferably within 6 months, and  
15 where step d) follows step c) or starts simultaneously  
with step d).

16 17. A polymer substrate metallized according to the  
method of each of the preceding claims 1-16.



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>C23C 18/20, 14/20, 18/54, C25D 5/56</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 00/20656</b> <b>(43) International Publication Date:</b> 13 April 2000 (13.04.00)
<b>(21) International Application Number:</b> PCT/DK99/00523 <b>(22) International Filing Date:</b> 4 October 1999 (04.10.99) <b>(30) Priority Data:</b> PA 1998 01247 ✓ 2 October 1998 (02.10.98) DK <b>(71) Applicant (for all designated States except US):</b> N.K.T. RESEARCH CENTER A/S [DK/DK]; Priorparken 878, DK-2605 Brøndby (DK). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> GLEJBØL, Kristian [DK/DK]; Fiskerhusene 8, DK-2620 Albertslund (DK). WINTHER-JENSEN, Bjørn [DK/DK]; Hornemannsgade 17, DK-2100 Copenhagen Ø (DK). <b>(74) Agent:</b> HOFMAN-BANG & BOUTARD, LEHMANN & REE A/S; Hans Bekkevolds Allé 7, DK-2900 Hellerup (DK).		<b>(81) Designated States:</b> AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the</i> <i>claims and to be republished in the event of the receipt of</i> <i>amendments.</i>
<b>(54) Title:</b> A METHOD OF METALLIZING THE SURFACE OF A SOLID POLYMER SUBSTRATE AND THE PRODUCT OBTAINED		
<b>(57) Abstract</b>  A method of metallizing a solid polymer substrate comprising the steps of: a) generating radicals on the substrate surface by subjecting it to a gas plasma, b) forming a layer on the surface using a plasma enhanced polymerisation process employing one or more monomers comprising monomers selected among cyano acrylate, mono- and diacrylates, such as acrylic acid, triethylen glycol diacrylate, glycidyl acrylate, isocyanates, such as 1,4-diisocyanobutane, toluenediisocyanate, epoxy compounds, such as glycidyl methacrylate, preferably 2,3-epoxypropyl methacrylate, allylic and vinylic compounds, such as vinyl acetic acid, vinyl norbonene, vinyl pyrrolidone, vinyl trimethoxysilane, vinyl trimethylsilane allylene, allyl alcohol, allyloxymethylsilane, allylphenol, allylurea 1-allylthiourea(thiosineamine), c) providing a short surface deposition using a PVD or CVD process to deposit metal atoms, such as copper, tin, silver palladium, platinum, or gold, and d) optionally providing a metallization of the surface by using a conventional electroless bath, or avoiding electroless metallization by using direct electrolytic metallization, when the metal layer formed in c) has a thickness allowing electrolytic metallization.		

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A method of metallizing the surface of a solid polymer substrate and the product obtained

- 5 The present invention relates to a method of metallizing the surface of polymer substrates such as polyolefins, fluorine containing polymers, polyalkylenes, polyarylenes and mixtures thereof and the product obtained.
- 10 Polymer surfaces with low surface energy such as untreated or unmodified polymer substrates are in general difficult to metallize using conventional methods based on electroless or galvanic plating methods.
- 15 One approach to obtain metallization on polymer surfaces is given in US 3,801,368, based on the fact that an electroless plating from a solution can be carried out, provided that the surface is first doped using noble metals like Au or Pt. The doping of the surface with noble met-
- 20 als prior to plating is, according to US 3,801,368, carried out by a vacuum evaporation or sputtering process. The advantage of using this type of process is that the energy of the metal-atoms hitting the surface often is sufficient to ensure a good bonding between the subse-
- 25 quently plated metal-film and the polymer surface.

The method described in US 3,801,368 is not universally applicable, but limited to certain polymers. Prior to the doping of the surface by noble metals, it is thus often

30 necessary to modify the chemical composition of the surface, in order to obtain sufficient adhesion between the subsequently plated film and the polymer surface.

The required change of chemical composition, or surface

35 treatment, depends on the substrate to be treated. Corona treatment is widely employed. The corona discharge con-

sists of a number of small sparks created between the substrate surface and a counter electrode (a silent discharge). Most often this treatment is carried out in ambient atmosphere, and results in erosion of the surface as well as in a generation of free radicals due the energy density of the discharges and the reactivity of the atmosphere. One of the problems regarding this method is, that it is not suited for treatment prior to metallizing strongly curved surfaces or surfaces with many cavities. Other problems relate to the limited control over the resulting chemical composition of the surface.

Often a simple corona treatment is not sufficient and more specialised methods has to be employed to ensure a sufficient adhesion.

One possible method is described in WO 97/37844, where a method to obtain a coupling layer between the surface to be plated and the plated metal-film is described. According to WO 97/37844, the coupling layer is formed by vacuum deposition of a monomer on the surface, which is subsequently polymerised by an irradiation process. To ensure a good coupling between the surface and the coupling layer, and between the coupling layer and the plated metal film, plasma-treatment can be used. This process is especially suited for treatment of polymer films of infinite lengths, as the different processes (plasma-treatment, deposition of coupling layer and polymerisation of coupling layer) are carried out at different, separate, stations.

The nature of this process makes it furthermore not suitable for treatment of fluorine containing polymers like poly-tetra-flour-ethylene (PTFE).

A number of patents describe methods for electroless plating of PTFE. In JP 92-240189 a PTFE substrate is irradiated with UV laser in the presence of amine or amide followed by an immersing in an electroless metal plating bath. This results in a good bonding of the plated metal to the substrate. However, this method is very difficult to control and also very expensive.

US 3,956,535 discloses a further method of metallization where the object to be metallized is coated with a film having incorporated therein a hydrolysed metal complex. Upon this metal complex a metal or metal ion is adsorbed and acts as catalyst for autocatalytic metal deposition. This method is not usable on many types of polymer substrates due to poor adhesion between the coated film and the substrate.

Also US 4,952,286 describes a method which includes immersing an article to be plated into an electrolytic bath containing dissolved plating metal. Before immersing, the surface has been provided with areas of catalytic metal chalcogenide coating to be converted to a chemical resistant metal-coating.

US 4,057,663 describes a method to make hydrophobic polymers suitable for electroless plating using a concentrate containing  $P_2O_5$ . This method is particularly suitable for polymers containing fluor, but not very useful for other polymers.

US 4,919,768 discloses another expensive method of metallization, where non-conducting surfaces are provided with a metal sulphide coating, acting as a base for direct electroplating.

Common to the above mentioned methods are, that they are either very expensive, complicated to use or not applicable to various types of polymer substrates.

- 5 The object of the present invention is to provide an industrially applicable method of binding a metal layer to a polymer substrate, which method does not comprise the above mentioned problems, resulting in good binding strength, and can be used on most polymer substrates.

10

Another object of the present invention is to provide a fast method of binding a metal layer to a polymer surface, and thereby provide a good binding strength.

- 15 A further object of the present invention is to provide a method of metallizing a polymer surface, which does not result in any severe depolymerisation of the polymer substrate, in particular when the substrate material exhibits fluorine and/or tertiary carbon atoms, and by use of  
20 which method the surface affinity against the metal is improved.

- A further object of the present invention is to provide a metallized polymer surface, which can be enhanced by  
25 electrochemical deposition using any conventional method.

Another object of the present invention is to provide a method for metallizing a polymer substrate, which method is economical acceptable.

30

A further object of the present invention is to provide a method for metallizing a polymer substrate, which method is uncomplicated to use.

These objects are achieved by a method of metallizing a surface of a solid polymer substrate comprising the steps of

- 5 a) generating radicals on the substrate surface by subjecting it to a gas plasma,
  - b) forming a layer on the surface using a plasma enhanced polymerisation process employing one or more monomers  
10 comprising monomers selected among cyano acrylate, mono- and diacrylates, such as acrylic acid, triethylen glycol diacrylat, glycidyl acrylat, isocyanates, such as 1,4-diisocyanobutane, toluenediisocyanate, epoxy compounds, such as glycidyl methacrylate, preferably 2,3-epoxypropyl  
15 methacrylat, allylic and vinylic compounds, such as vinyl acetic acid, vinyl norbonene, vinyl pyrrolidone, vinyl trimethoxysilane, vinyl trimethylsilane allylene, allyl alcohol, allyloxymethylsilane, allylphenol, allylurea 1-allyltheourea(thiosine-amine), vinyl-amine, vinyl-alcohol  
20 or allyl-amine.
  - c) providing a short surface deposition using a PVD or CVD process to deposit metal atoms, such as copper, tin, silver palladium, platinum, or gold  
25
  - d) optionally providing a metallization of the surface by using a conventional electroless bath, or  
avoiding electroless metallization by using direct elec-  
30 trolytic metallization, when the metal layer formed in c) has a thickness allowing electrolytic metallization.
- Step b) may start before step a) provided that step b) does not terminate until step a) is started, simultane-  
35 ously with step a), under step a), or follow immediately after step a). Step c) may start before step b), simulta-



neously with step b), follow immediately after step b) or within 8 months after step b), preferably within 6 months, and step d) may follow step c) or start simultaneously with step d).

5

The method is preferably carried out in a reactor at least partly evacuated from air and water vapour. Further, the reactor should have a channel for feeding the working gas, and a channel for feeding the monomer or monomer mixture. The monomer or monomer mixture is introduced as a gas, e.g. by evaporation from a bottle.

Gas is fed into the reactor, and the plasma is generated (step a). Before, simultaneously or shortly thereafter monomer or monomer mixture is fed into the reactor (step b).

It is noted that the polymerisation preferably should be carried out at plasma discharge parameters resulting in a surface containing chemical groups promoting acid-base reactions with the subsequently deposited metal layer.

The generation step a) is preferably, as stated in claim 11, carried out for a period of between 0.01 and 1000 seconds, preferably between 1 and 500 seconds, more preferably between 10 and 60 seconds, and the treatment step b) is preferably carried out for a period of between 0.1 and 1000 seconds, preferably between 1 and 500 seconds, more preferably between 10 and 200 seconds.

The treatment step b) may continue when step a) has ended, even though there no longer are generated radicals on the substrate surface. This continuation of step b) will then result in a polymerisation of monomers onto the

new polymeric layer which already have been bound to the polymer surface.

If the surface of the polymer substrate is contaminated  
5 with water, oil or other contaminants, step a) is preferably carried out for more than 30 seconds, and step b) is started 10 to 30 seconds after step a) so as to clean the surface before the monomers are polymerised onto the substrate surface.

10

The partial pressure of the gas or the plasma in step a) is preferably between 0.1 and 10000 Pa.

The monomer pressure in step b) is preferably, as stated  
15 in claim 10, between 0.1 and 10000 Pa, more preferably between 10 and 1000 Pa.

The temperature is not important but should preferably, as stated in claim 14, be the same under both step a) and  
20 step b) and preferably the temperature under both step a) and step b) is between 250 and 450 K, most preferably between 280 and 330 K.

The total pressure, i.e. the sum of the partial pressures  
25 of the air, optionally water vapour, the gas or plasma and the monomer, under step a) is preferably, as stated in claim 15, equal to the total pressure under step b), the total pressure is preferably between 0.2 and 100000 Pa, more preferably between 0.2 and 10000 Pa, and most  
30 preferably between 10 and 1000 Pa.

The polymer substrate can be any polymer material provided that free radicals are created on the surface of the material when it is subjected to a gas plasma or  
35 other means of radical generation.

Preferably, as stated in claim 6, the polymer substrate is a polyolefine type, such as PE, PP, or an aryl type, such as styrene, a diene type, such as polybutadiene, polyisoprene, a silicone type, such as silicone rubber, a  
5 fluorine type, such as polytetrafluorethylene or its copolymers.

The substrate can have any shape and any size, and may comprise complicated geometries. Preferably the polymer  
10 substrate is in the form of film, sheet, pipe, rod, porous or non-porous body, fabric, non-woven fabric, fibres or threads and/or as profiles made by extrusion, compression moulding, injection moulding, thermoforming or vacuum forming.

15 The generation of radicals on the substrate surface is preferably obtained by subjecting the substrate to a plasma discharge.

20 The plasma can be generated by any known methods, but preferably, as stated in claim 9, the gas plasma is generated by excitation of a gas in a direct current (DC), low frequency (LF), radio frequency (RF) or microwave (MW) generated electric field. Most preferably the gas  
25 plasma is generated by excitation of a gas in a direct current (DC) or by excitation using low frequency (LF).

The intensity of the used gas plasma should preferably have a level ensuring creation of radicals in the polymer  
30 surface. If the level is too high, this may result in severe damage of the bulk-polymer (depolymerisation). Hence, the power level of the plasma should be optimised so that surface radicals are created, but no serious damage is made to the bulk.

35

A preferred method of generating a plasma discharge is described in the applicant's European patent application No. EP 96610018.2.

- 5 Preferred embodiments for the invention are specified in claims 2 - 15.

10 *Experimental systems*

Although it is possible to carry out all necessary steps in a single vacuum vessel, initial experiments were carried out in two separate systems. In one of the systems  
15 the virgin polymer surface was altered by the use of a plasma treatment using a working gas and monomers. In the other vacuum system metal atoms were subsequently deposited to the surface of the test samples. Although possible in an industrial production, the approach of using  
20 separate machines for the two steps is highly inefficient. The results obtained from these experiments do, however, reflect the results obtainable if a custom made system, able to perform both tasks is used.

- 25 The first step was on all samples carried out in an experimental plasma system, essentially consisting of a 22 litre vacuum vessel having two inlet channels for gas and for monomer, respectively, and an electrode arrangement as described above with reference to the applicant's EP  
30 application No. 96610018.2 The plasma is generated using the 3-phase technique described above with a frequency of 50 Hz and  $U_0$  of 240 to 280V. 27 electrodes are arranged in a circle around the vacuum vessel with a diameter of 17 cm. Every third of the electrodes is connected to  $U_r$ ,  
35 another every third of the electrodes is connected to  $U_s$ ,

and the last every third of the electrodes is connected to  $U_t$ .

The second step was on all samples carried out in an experimental plasma system, essentially consisting of a glass bowl having an internal volume of 15 litres. To atomise the metal and transfer it from the target to the sample surface a custom made magnetron was constructed. The magnetron is essentially a copper plate, having a diameter of 10 cm and a thickness of 4 mm. The back-side of the copper plate is shielded using a ceramic container. On the backside of the copper-plate a magnet is mounted. The magnetron is operated by applying a negative DC potential of 450 V. During operation a current of 0.05 A is drawn between the magnetron and the positive parts of the chamber. During all experiments argon is used as the working gas for the magnetron.

Both plasma systems are pumped using the same vacuum system comprising an Edwards EH 250 Roots-blower, backed by an Alcatel rotary vane pump. The pressure is monitored using an Alcatel pirani-gauge, mounted on the start of the pumping-line.

During step a) and b) the sample is held at floating potential.

#### Example 1

Covering a 100x50x3 mm sheet of polytetrafluorethylene (PTFE) with a conductive layer of metal.

#### Step 1

The sheet was subjected to an argon plasma discharge, generated as described above, for 20 s at a pressure of

0.1 mbar. Hereafter a vapour essentially comprising of 2-ethyl cyano acrylate and glycidylmetacrylate was let into the argon plasma at a pressure of 0.15 mbar for 30 s.

5     Step 2

After this treatment 100 nm of silver (Ag) was deposited onto the surface, making the surface conductive. The deposition was accomplished by using a silver sheet as a target on the magnetron, and the magnetron was operated  
10    for 60 seconds.

Step 3

After Ag deposition, the sheet was immersed in an electroless copper bath, ("Shipley Cuposit 251 electroless copper"). Due to the combined treatment in step 1 and 2  
15    an adherent copper coating was formed where Ag was deposited.

The copper layer can be 0.5  $\mu\text{m}$  or more, depending on the  
20    treatment time in the electroless copper bath. The average thickness obtained after a given time is as claimed by Shipley 2.5  $\mu\text{m}$  per hours.

The adhesion strength of the copper layer was examined by  
25    the standard well known to people skilled in the art, DIN 53 151 having a scale from GT 0 to GT 5, where zero is excellent. The treated sample in this example complied the standard and got the score Gt 0 - Gt 1.

30    Example 2

Covering of a component made from polypropylene (PP) with a shielding metallic layer.

## Step 1

The component was subjected to an argon plasma as described above for 10 s at a pressure of 1 mbar. Hereafter a vapour essentially comprising of toluene-2,4-diisocyanate was let into the plasma chamber at a pressure of 2 mbar for 20 s.

## Step 2

After this treatment 2 ML (monolayers) of platinum (Pt) was accomplished by using a Pt sheet as a target on the magnetron, and the magnetron was operated for 5 seconds.

## Step 3

The component was immersed in an electroless copper bath, ("Shipley Cuposit 251 electroless copper"). Due to the combined treatment in steps 1 and 2 an adherent copper coating was formed where Pt was deposited on the PP component.

20 Example 3

Covering a PTFE surface with a 0.5  $\mu\text{m}$  metal layer.

Steps 1 and 2 were conducted as described in example 2.

25

## Step 3

The component was immersed in an electroless copper bath, ("Shipley Cuposit 251 electroless copper"). Due to the combined treatment in steps 1 and 2 an adherent copper coating was formed where Ag was deposited.

30

Example 4a

35 Covering a PTFE surface with a 5  $\mu\text{m}$  metal layer.

Steps 1 - 2 identical to the steps in example 2.

Step 3

Copper was then deposited on the Ag covered surface using  
5 a conventional electroplating technique.

Example 4b

Covering a PTFE surface with a 5  $\mu$ m metal layer

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Steps 1 - 3 identical to the steps in example 3

Step 4

More copper was then deposited on the surface using a  
15 conventional electroplating technique.



## CLAIMS.

1. A method of metallizing a solid polymer substrate comprising the steps of

5 a) generating radicals on the substrate surface by subjecting it to a gas plasma,

10 b) forming a layer on the surface using a plasma enhanced polymerisation process employing one or more monomers comprising monomers selected among cyano acrylate, mono- and diacrylates, such as acrylic acid, triethylen glycol diacrylate, glycidyl acrylate, isocyanates, such as 1,4-diisocyanobutane, toluenediisocyanate, epoxy compounds, 15 such as glycidyl methacrylate, preferably 2,3-epoxypropyl methacrylate, allylic and vinylic compounds, such as vinyl acetic acid, vinyl norbonene, vinyl pyrrolidone, vinyl trimethoxysilane, vinyl trimethylsilane allylene, allyl alcohol, allyloxymethylsilane, allylphenol, allylurea 20 1-allyltheourea(thiosineamine),

25 c) providing a short surface deposition using a PVD or CVD process to deposit metal atoms, such as copper, tin, silver palladium, platinum, or gold, and

d) optionally providing a metallization of the surface by using a conventional electroless bath, or

30 avoiding electroless metallization by using direct electrolytic metallization, when the metal layer formed in c) has a thickness allowing electrolytic metallization.

2. A method according to claim 1, wherein the catalytic metal comprises Pt, Ag, Pd, Cu and Au.

3. A method according to claim 1, wherein the monomer or monomer mixture comprises one or more of cyanoacrylate and glycidyl metacrylate, preferably 2,3-epoxypropyl methacrylate.

5

4. A method according to each of the preceding claims 1, 2 or 3, wherein step b) comprises treatment of the surface with a monomer vapour comprising 0.5 to 90 mole-%, preferably between 10 and 60 mole % of 2-ethyl cyano acrylate vapour.

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5. A method according to claim 4, wherein the monomer prior to the vaporisation consists essentially of 2-ethyl cyano acrylate, an acid having a partial vapour pressure in the plasma which is lower than the partial vapour pressure of 2-ethyl cyano-acrylate, and up to 40 weight-% of another filler, preferably an acid having a partial vapour pressure in the plasma which is lower than half the partial vapour pressure of 2-ethyl cyano-acrylate, most preferably the acid is a polyphosphoric acid and is present prior to the vaporisation in a concentration up to 10 weight-%.

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6. A method according to each of the preceding claims, wherein the polymer substrate is a polyolefine type, such as PE, PP, or an aryl type, such as styrene, a diene type, such as polybutadiene, polyisoprene, a silicone type, such as silicone rubber, a fluorine type, such as polytetrafluorethylene or its copolymers.

25

30

7. A method according to each of the preceding claims 1-5, wherein the polymer substrate is a PTFE and PP.

8. A method according to each of the preceding claims, wherein the polymer substrate is an injection moulded

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polymer component, a polymer fibre, a polymer thread or a polymer filler.

9. A method according to each of the preceding claims,  
5 wherein step a) comprises the generation of radicals by use of a gas plasma generated by excitation of the gas in a direct current (DC), low frequency (LF), audio frequency (AF), radio frequency (RF) or microwave generated electric field.

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10. A method according to each of the preceding claims, wherein the monomer pressure in step b) is between 0.1 and 100000 Pa, preferably between 10 and 1000 Pa.

11. A method according to each of the preceding claims,  
15 wherein the generation step a) is carried out for a period of between 0.01 and 1000 seconds, and the treatment step b) is carried out for a period of between 0.1 and 1000 seconds.

20

12. A method according to claim 11, wherein step a) is carried out for more than 30 seconds, and step b) is started 10 to 30 seconds after step a).

13. A method according claim 11, wherein the generation  
25 step a) is carried out for a period of between 10 and 60 seconds, and the treatment step b) is carried out for a period of between 10 and 200 seconds.

14. A method according to each of the preceding claims,  
30 wherein the temperature is the same under both step a) and step b), and preferably the temperature under both step a) and step b) is between 250 and 450 K, most preferably between 280 and 330 K.

35

15. A method according to each of the preceding claims, wherein the total pressure under step a) is equal to the total pressure under step b), the total pressure is preferably between 0.2 and 100000 Pa, more preferably between 0.2 and 10000 Pa, and most preferably between 10 and 1000 Pa.

16. A method according to claim 1, where step b) starts before step a) provided that step b) does not terminate until step a) is started, simultaneously with step a), under step a), or follows immediately after step a), where step c) starts before step b), simultaneously with step b), follows immediately after step b) or within 8 months after step b), preferably within 6 months, and where step d) follows step c) or starts simultaneously with step d).

17. A polymer substrate metallized according to the method of each of the preceding claims 1-16.

A method of metallizing the surface of a solid polymer substrate and the product obtained

ABSTRACT

5

A method of metallizing a solid polymer substrate comprising the steps of

10 a) generating radicals on the substrate surface by subjecting it to a gas plasma,

b) forming a layer on the surface using a plasma enhanced polymerisation process employing one or more monomers comprising monomers selected among cyano acrylate, mono-  
15 and diacrylates, such as acrylic acid, triethylen glycol diacrylate, glycidyl acrylate, isocyanates, such as 1,4-diisocyanobutane, toluenediisocyanate, epoxy compounds, such as glycidyl methacrylate, preferably 2,3-epoxypropyl methacrylate, allylic and vinylic compounds, such as vi-  
20 nyl acetic acid, vinyl norbonene, vinyl pyrrolidone, vinyl trimethoxysilane, vinyl trimethylsilane allylene, allyl alcohol, allyloxymethylsilane, allylphenol, allylurea 1-allyltheourea(thiosineamine),

25 c) providing a short surface deposition using a PVD or CVD process to deposit metal atoms, such as copper, tin, silver palladium, platinum, or gold, and

30 d) optionally providing a metallization of the surface by using a conventional electroless bath, or

avoiding electroless metallization by using direct electrolytic metallization, when the metal layer formed in c) has a thickness allowing electrolytic metallization.

35

## PATENT COOPERATION TREATY

## PCT

## INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference <b>P199800998 WO</b>	<b>FOR FURTHER ACTION</b> see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. <b>PCT/DK 99/ 00523</b>	International filing date (day/month/year) <b>04/10/1999</b>	(Earliest) Priority Date (day/month/year) <b>02/10/1998</b>
Applicant <b>N.K.T. RESEARCH CENTER A/S et al.</b>		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

## 1. Basis of the report

- a. With regard to the language, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

- b. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international search was carried out on the basis of the sequence listing :

☐ contained in the international application in written form.

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☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ Certain claims were found unsearchable (See Box I).

3. ☐ Unity of invention is lacking (see Box II).

## 4. With regard to the title,

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

## 5. With regard to the abstract,

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☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

## 6. The figure of the drawings to be published with the abstract is Figure No.

☐ as suggested by the applicant.

☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

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☐

None of the figures.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/DK 99/00523

## A. CLASSIFICATION OF SUBJECT MATTER

C23C18/20, C23C14/20, C23C18/54, C25D5/56

According to International Patent Classification (IPC) or to both national classification and IPC 7

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C23C, C25D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 97/37844 A (SIGMA LABORATORIES OF ARIZONA, INC.) 16 October 1997, the whole document. --	1-17
A	EP 0640474 A (FRAUNHOFER-GESELLSCHAFT ZUR FÖRDERUNG DER ANGEWANDTEN FORSCHUNG E.V.) 01 March 1995, the whole document. --	1-17
A	US 5288541 A (BLACKWELL ET AL.) 22 February 1994, the whole document. --	1-17
A	DATABASE WPI, week 198935,	1

☒ Further documents are listed in the continuation of box C.

☐ Patent family members are listed in annex.

### \* Special categories of cited documents:

- \* A\* document defining the general state of the art which is not considered to be of particular relevance
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- \* O\* document referring to an oral disclosure, use, exhibition or other means
- \* P\* document published prior to the international filing date but later than the priority date claimed

- \* T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \* X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \* Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- \* &\* document member of the same patent family

Date of the actual completion of the international search

25 January 2000

Date of mailing of the international search report

14.03.00

Name and mailing address of the ISA

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# INTERNATIONAL SEARCH REPORT

Intern. Application No

PCT/DK 99/00523

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	<p>Derwent Publications Ltd.,  London, GB, Class G11B,  AN 1989-252964;  &amp; JP 01 184741 A (FUJITSU  LTD) 27 July 1989,  abstract.</p> <p>-----</p>	



**ANHANG**

Zum internationalen Recherchenbericht über die internationale Patentanmeldung Nr.

**ANNEX**

To the International Search Report to the international Patent Application No.

**ANNEXE**

Au rapport de recherche international relatif à la demande de brevet international n°

**PCT/DK 99/00523 SAE 250331**

In diesem Anhang sind die Mitglieder der Patentfamilien der im obengenannten internationalen Recherchenbericht angeführten Patentdokumente angegeben. Diese Angaben dienen nur zur Unterrichtung und erfolgen ohne Gewähr.

This annex lists the patent family members relating to the patent documents cited in the above-mentioned search report. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

La présente annexe indique les membres de la famille de brevets relatifs aux documents de brevets cités dans le rapport de recherche international visée ci-dessus. Les renseignements fournis sont donnés à titre indicatif et n'engagent pas la responsabilité de l' Office.

Im Recherchenbericht angeführte Patentdokumente Patent document cited in search report Document de brevet cité dans le rapport de recherche			Datum der Veröffentlichung Publication date Date de publication		Mitglied(er) der Patentfamilie Patent family member(s) Membre(s) de la famille de brevets		Datum der Veröffentlichung Publication date Date de publication	
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					US	A	5895723	20-04-1999
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